DEVELOPMENT OF GALVANIC COATING (ZINC) FOR APPLICATION IN MILS STEEL UPON CORROSIVE ENVIRONMENT

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RESEARCH VOTE NO: RDU 151308 UNIVERSITI MALAYSIA PAHANG

DEVELOPMENT OF GALVANIC COATING (ZINC) FOR APPLICATION IN MILS STEEL UPON CORROSIVE ENVIRONMENT

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Final report submitted in partial fulfilment of the requirements to close the grant of RDU 151308

Faculty of Chemical Engineering and Natural Resources UNIVERSITI MALAYSIA PAHANG

APRIL 2017

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ACKNOWLEDGEMENT

Thanks to Allah S.W.T for giving me so much health and opportunity to gain thousands of knowledge and experience to complete this Final Report Research Project. This corner is the place where I can express my gratitude towards Ministry of Education Malaysia for funding this research activity.

Besides, my sincere appreciation also to the Chemical Engineering Laboratory, Faculty of Chemical Engineering and Natural Resources, Universiti Malaysia Pahang for the availability of the equipment and facilities. I would like to extend my gratitude to team members who have put in the effort to always help and guided with valuable advice during this research period. Thank you for sharing those experiences and knowledge. To my dear students whom openhandedly work out the research plan accordingly to make this project successful, thank you so much.

Last but not least, the support I received from my family who are contributing in term of mentally to this project was vital for the success of the project. I am grateful for their constant support and help.

ABSTRACT

Organic coated steel is widely used in industry because of well-known of its advantage towards corrosion protection. The objective is to understanding the physical appearances and behaviour of formulated organic coating and commercialized spray using SEM by investigating the internal reaction and environment nature. Pigment volume concentration of formulated organic coating was varied as 10, 20 and 30 % to evaluate the effectiveness of coatings towards corrosion protection. There were four methods to identify the effectiveness of organic coating by adhesion test, immersion test, polarization test and thickness of the different layer (1, 3, 5 layers). In addition, the kinetic growth can be analyzed or interpret by using scanning electron microscope (SEM) for morphology observation. First, the samples were coated with the coating (commercialized spray and formulated organic coating). The 'dry-on-dry' technique was implemented on these samples during painting or coating on the samples. After that, the samples were immersed in 3.5 % NaCl solution in duration at least 60 days. The thickness was measured by weighing before and after coating. The image of the sample for immersion test was taken from SEM analysis. The result of adhesion test for epoxy and zinc-epoxy shows high strength in chemical bonding. Lastly, the polarization test was takes place to determine the parameters of corrosion. The aim is to evaluate the efficiency of organic coating towards corrosion protection. The sample from formulated organic coating (10% PVC) show the highest corrosion rates, 0.00018 mm/yr. The formulation coating provides barrier protection while commercialized spray provides both galvanic and barrier protection from corrosion.

ABSTRAK

Organik keluli bersalut digunakan secara meluas dalam industri kerana terkenal kelebihan ke arah perlindungan kakisan. Objektifnya adalah untuk memahami penampilan fizikal dan tingkah laku salutan organik digubal dan semburan dikomersialkan menggunakan SEM dengan menyiasat tindak balas dan persekitaran alam semula jadi dalaman. Pigmen kepekatan jumlah salutan organik dirumuskan telah diubah seperti 10, 20 dan 30% untuk menilai keberkesanan lapisan untuk perlindungan kakisan. Terdapat empat kaedah untuk mengenal pasti keberkesanan salutan organik oleh ujian melekat, ujian rendaman, ujian polarisasi dan ketebalan lapisan yang berbeza (1, 3, 5 lapisan). Selain itu, pertumbuhan kinetik boleh dianalisis atau mentafsir dengan menggunakan mikroskop elektron pengimbas (SEM) untuk pemerhatian morfologi. Pertama, sampel telah disalut dengan salutan (semburan dikomersialkan dan lapisan organik dirumuskan). Teknik 'kering-on-kering' telah dilaksanakan pada sampel tersebut sepanjang lukisan atau salutan pada sampel. Selepas itu, sampel telah tenggelam dalam 3.5% larutan NaCl dalam tempoh sekurang-kurangnya 60 hari. ketebalan diukur dengan menimbang sebelum dan selepas salutan. Imej sampel untuk ujian rendaman diambil daripada analisis SEM. Keputusan ujian lekatan untuk epoksi dan zink epoksi menunjukkan kekuatan yang tinggi dalam ikatan kimia. Akhir sekali, ujian polarisasi itu berlaku untuk menentukan parameter hakisan. Tujuannya adalah untuk menilai kecekapan salutan organik ke arah perlindungan kakisan. Sampel dari salutan organik dirumuskan (10% PVC) menunjukkan kadar kakisan tertinggi, 0.00018 mm / tahun. Lapisan penggubalan menyediakan perlindungan halangan manakala semburan dikomersialkan menyediakan kedua-dua perlindungan galvani dan halangan daripada kakisan.

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CHAPTER 1

INTRODUCTION

1.1 MOTIVATION

Preservation of metals in their pure form from corrosion can be achieved only through proper protection. One of the possible method is preservation by organic zinc coating. This method is recognized as the most convenient method and has been demonstrated to be more effective than others method. Basically, it will ensure both chemical and electrochemical reaction between anticorrosion pigments and the metal or a corrosion environment penetrating the coating. Due to easy handling, zinc coating can be done on any type and shape of substrates. The coating also shows very uniform surface, thus having high wear resistance.

The problem lies on the ideal thickness to be suit for metallic structures and adhesively with the coated substrate. Hence, it can be suggested by providing a graded coating with the combination different strength, hardness and wear resistance at difference coating thickness. The properties of the coating can be controlled by controlling the composition of the pigments. This can be achieved by adjusting the volume percentage of zinc pigments. The composition of fly ash as an extender pigments also contributes in this research. The addition of extender pigments in the coating will reduced the cost of coating because the consumption of zinc will be decreased.

1.2 OBJECTIVE

The objective of this study are as below:

- 1.3.1 to study the effect of organic zinc coating and commercialized spray on steel as well as its properties such as corrosion resistance, wear resistance and thickness,
- 1.3.2 to study the effect of pigment volume concentration (PVC) in the coating,
- 1.3.3 to establish the correlation between the performance of the designed coating and metallic properties.

1.3 SCOPES

A few scopes are identified in order to achieve the objectives. They are:

- 1) Preparation of the metallic samples from a pure iron sheets.
- Grinding process of fly ash will be done in order to get very fine particles of fly ash
- The formulation of coating based on pigment volume concentration and composition of an extender pigments.
- 4) Studying the internal behaviour of coating, cracking or failure because of corrosion using SEM analysis for morphology observation.
- 5) In immersion test using 3.5 % NaCl aqueous solution, open to air and held at temperature room (25 °C) for 60 days.
- 6) Electrochemical polarization curve measurements will be used to study corrosion behavior of coated substrates at various coating thickness.

1.4 RATIONALE AND SIGNIFICANCE

This study will give a significant result between the commercialized spray and formulated organic coating. The study on the thickness of the coating is to fill in the gap of the previous research. The utilization of the extender pigment which are clay and kaolin, helps to minimize the used of zinc oxide as pigment in the coating, thus change the kaolin from waste to wealth.

THESIS OVERVIEW

The structure of the reminder of the thesis is outlined as follow:

Chapter 2 provides a description of paint coating and its applications in industry. The principle of the system and how paint coatings works are described in this chapter. Moreover, this chapter also provides a brief discussion of the coatings materials available for the effectiveness of organic coating towards corrosion protection. A brief discussion on methods of coatings is also provided.

In addition, a summary of the previous experimental work on the effect of using different coatings is also presented. Chapter 3 discuss the methods used in the preparing the paint coating on carbon steel. Then, test using several methods is presented and a few equations that can be used in the numerical calculations are presented. Chapter 4 presents the result obtained from the experiments while chapter 5 stated the conclusion.

CHAPTER 2

LITERATURE REVIEW

2.1 CORROSION IN OUR LIFE

The increasing industrialization in our life is concomitant with the ever-growing number of metals that corrode and becomes devalued (Kalendova *et al.*, 2006). The corroded metal is actually the product of corrosion process. Corrosion is a natural phenomenon occurred when metal, usually obtained from the salts, is being exposed to the water, carbon dioxide and oxygen in the air; thus transfer to a more energetically convenient state; i.e. it transforms into the form of an oxide or known as rust. Corrosion comes in a lot of form and can be classified by the cause of the chemical deterioration of a metal since it destroys the beauty of object and shorten its life (Terence, 2015). Table 2-1 below shows several types of corrosion.

Table 2.1-1: Types of corrosion

Types of corrosion	Description
Uniform corrosion	The reaction starts at the surface and proceeds
	uniformly.
Localized corrosion	The basis metal is eaten away and perforated in
(pitting corrosion)	places in the manner of holes, the rest of the surface being
	affected only slightly or not at all.
Wide pitting	The corrosion causes localized scarring.
corrosion	



The corrosion failure of engineering materials has brought a great deal of economy loss, so that more researchers have focused on the study of corrosion behavior and mechanism of metal materials to find better protective methods and technologies (Rousseau *et al.*, 2009) and (Rios *et al.*, 2014). It is a must know knowledge that corrosion can only attack on the surface of the metal, hence any modification of the surface or its environment will shift the rate of corrosion.

Table 2-2 below can be a basis of designing the protection method of metal from corrosion where it shows several different concepts by which surface rate of reaction can be reduced.

	Concept			-	Ind	lustrial Proc	ess	
	Removal of oxidizing	agent		Boiler	water tre	eatment		
	Prevention of	surface		Cathod	lic protec	ction - sacrifi	cial and	ode
reactio	n					- impre	ssed cu	rrent
				Anodic	e protecti	ion		
	Inhibition of	surface		Chemi	cal inhib	itors		
reactio	n			pH con	trol			
	Protective coatings:							
-	Organic			Paint				
				Claddii	ngs			
-	Metallic			Electro	plating			
		Galvanising						
		Metal spraying						
-	Non-metallic		Anodising					
			Conversion coatings					
	Modification of the m	netal	Alloys - stainless steel					
			- cupronickel					
					- high te	emperature al	loys	
	Modification of	surface		Mainte	nance to	remove corr	osive a	gents
condit	ions			Design	to avoid	d crevices		
			Design to avoid reactive metal					
		combinations						

 Table 2.1-2: Corrosion protection techniques

Source: (Graeme, 2008)

2.2 ORGANIC COATING

Throughout proper protection, preservation of metals in their pure form can be achieved. One of the possible methods is protection by organic coating (Funke, 1997), (Kalendova *et al.*, 2004) and (Schoff, 2005) which ensures both a chemical and electrochemical reaction between an anticorrosion pigment and the metal or a corrosion environment penetrating the coating (del Amo *et al.*, 2004). Organic coatings are most popular method and widely used in protection of metallic materials (Rajiv and Kopinski, 2009), (Rosales *et al.*, 2004) and (Puomi and Fagerholm, 2001). The organic binder and inorganic pigments/fillers in this coatings provide barrier and active protection to the metal substrate from corrosion. The binder and filler in the organic coatings contribute to the barrier protection, while active protection is achieves from anticorrosive pigments (Liu *et al.*, 2016) and (Visser *et al.*, 2015). Organic coatings differ from inorganic coating only based on its type of binder used.

Organic coating is used as a medium to prevent the metallic structure lowering the corrosion rate. The function is to isolate the metal from the corrosive environment (Mak, n,d.). There is three organic coating component are pigment, additive, and solvent. The pigment is a substance that gives particular colour when it is present in it or added to it. In 1918, the white pigment replaced the white lead using titanium dioxide compounds (Historical Background, n,d.).

The difference of organic coatings and inorganic coatings shown in Table 2.3-1 below:

				Organ	ic	Inorganic		
Binder			Epoxy			Silicate		
	Perfo	rmanc		Organi	c zinc	Inorganic with		
es :			with	high	build	high-build epoxy		
	sea	coast	epoxy			Life: 15 years		
marine			Life:	13.5				

Table 2.2-1: Difference of organic and inorganic coating

with blast	years	
cleaning		
Abrasion	Low	High
Solvents	Low	High
Sunlight	Low	High
Top coats	Easier	No over
	(denser surface)	coating

Source: (Eddy, 2013)

2.2.1 Advantages of organic coating

Organic coatings are widely used in order to protect the metal against corrosion. The key feature of organic coatings is to evaluate the effectiveness of coatings towards corrosion protection. The advantages of organic coatings compared to the other coatings are:

- i. The hydrophobic organic film only water can slightly penetrate.
- ii. Good corrosion resistances and waterproof to water or air.

iii. Consistent quality of organic coated steel.

- iv. Smooth appearance and variety of metallic colour.
- v. Well-known in domestic appliance market and successfully used for white goods such as refrigerator, washing machines, small kitchen appliances (microwave oven)
- vi. Production of the different surface such as smooth, orange peel, grained, textured or embossed in the flexibility of the coil coating process.
- vii. Organic coated steel reduces company taxes (waste treatment eliminate) and insurance premium.
- viii. By painting the metallic subtract will enhance the protective ability of steel.
- ix. Powder thermoset coatings have zero volatile organic content (VOC) thus produce eco-friendly coatings.
- x. Organic coated steel can be recycled at the end of life cycle likes the other steel products.

xi. Human and environment do not involved with danger in various sectors such as construction, domestic appliances, and general industry when using the organic coated steel because new transformation has been developing to lower organic- solvent content.

2.3 BINDER

Binder is polymeric substance which function to hold the pigments to the surface of substrate. (Fragata *et al.*, 1987), (Amo and Giudice, 1990) and (Pereira *et al.*, 1990) verified that the importance of the nature of the binder used in the coatings. As mentioned before, organic coatings and inorganic coatings differ in the type of binder. Organic coating uses organic binder like epoxy (Wicks *et al.*, 1994), (Marchebois *et al.*, 2002), (Marchebois *et al.*, 2002), (Marchebois *et al.*, 2004), (Marchebois *et al.*, 2004), (Meroufel and Touzain, 2007), (Meroufel *et al.*, 2008), (Armelin *et al.*, 2010), (Hammouda *et al.*, 2011) and (Meng *et al.*, 2015), butyl and urethane (Zhou *et al.*, 2002), (Petrovi *et al.*, 2004), (Ashraf *et al.*, 2015), while inorganic coating use silicate as a binder.

2.3.1 Epoxy Resin

Epoxy is an organic molecule consists of oxirane groups. Oxirane groups is an oxygen atom bonded to two adjacent carbon atoms in roughly a triangular form. However, oxygen in this component is highly reactive than other organic groups. Next, epoxy also is known as glycidol ether because the internal reaction is linked to the rest of organic molecule through an ether linkage (Mattson, 2013).

Besides that, epoxy resin is a polymer and containing two or more oxirane groups with an organic molecule. In order to make epoxy resin, Bisphenyl A must react with diglycidol ether. Bisphenyl A is made from the reaction of phenol and acetone to form di or bis which mean two phenol (Mattson, 2013).



Figure 2.3-1: Epoxy Resin Formation

Epoxy resin is widely used in industry for a protective barrier against corrosion and cure by internally generated heat and a thermosetting resin. Resin and hardener are parts of epoxy systems. Furthermore, the cross-linkage between polymer and hardener plays an important role to make sure become solid. The advantage of epoxy resin is strength adhesion, excellent cohesion, tightly binding pigment and good protection of passive barrier (Mattson, 2013).

The advantages of epoxy are cure times by slowing it down or speed up. In addition, viscosity is changed by warming the resin or cooling down. Epoxy has an infinite shelf life, so it will not easily get expired and bad in the bottle. Besides, it has no odor and non-hazardous chemicals (Mattson, 2013).

2.3.2 Zinc rich epoxy paint immersed in 3.5 % NaCl

In 2011, zinc rich epoxy paint (ZRP) in 3.5 % NaCl solution have been studied to identify the protective behaviour mechanism for single coat solvent – based using EIS about 100 kHz to 10 mHz. The result obtained the barrier nature of ZRP films reinforced by zinc was still protected the substrate steel even the cathodic protection effect by Zn dust become weak (Hammouda et al., 2011). The increasing barrier resistance because the zinc corrosion product precipitate inside coating by blocking the pores around the zinc particles originated (Abreu et al., 1996).

Figure 2.4.2-1 below shows the structure formula was under conductive form for ZRP using FTIR spectral characterization (Hammouda et al., 2011).



Figure 2.3-2: Structural formula of zinc rich epoxy paint from FTIR spectra result

Source: (Hammouda et al., 2011)

Figure 2.4.2-2, shows the SEM image of zinc rich epoxy paint after immersed in 3.5 % NaCl solution with oxidation product. The "white corrosion" appear when involved oxidation of zinc coating with NaCl solution (Kalendova, 2000). The shape of spherical zinc - pigmented coating must be sealed to secure the subtract protection barrier (Hammouda et al., 2011).



Figure 2.3-3: SEM image of zinc rich epoxy

Source: (Hammouda et al, 2011)

Furthermore, figure 2.4.2-3 below is white rust occurs on galvanized steel. When the pH is higher with high conductivity water, the zinc surface will be attacked by white rust (white Rust, n.d.).



Figure 2.3-4: White rust on galvanized steel

The immersion test is used to test the effectiveness of corrosion protection towards metals. Besides, zinc particles provide a cathodic protection of steel substrate at least beginning immersion for solvent-based (ZRPs) (Hare, 1998). The barrier effect of the paint was reinforced by the formation of zinc rich product in long term protection (Morcillo et al., 1990). A high pigment concentration required above 60 % by volume in solvent-based (ZRPs) to ensure the good electrical contacts between zinc pigment and steel subtract (Vilche et al., 2002).

The advantages offered by organic zinc-rich coating lie in the galvanic protection afforded by the zinc content, with chemical and moisture resistance similar to that of the organic binder. To compared with inorganic coatings, organic coatings generally have low service performance, but more ease in tolerance of application and surface preparation make them more popular (Philip and Schweitzer, 2006). (Ashraf *et al.*, 2015) proved that epoxy resin can be used in formulation of nanocomposite and microcomposite both provided good adhesion, heat, thermal, mechanical and corrosion resistance. Epoxy resin have a good barrier protection. This is proved by (Shreepathi., 2010) when the zinc content in the coating is low (40% by weight), the coating provided good barrier protection mainly come from the epoxy resin.

2.4 ZINC AS A PIGMENT

Zinc metal particles (zinc powder) is one of the metal that has been used for many years as a ingredient in the anticorrosion organic coating. Zinc was known as good sacrificial protection long time ago. The first use of zinc powder in coatings was in the year 1840 for making use of its high covering capacity without knowledge of its electrochemical properties of high anticorrosion efficiency to improve the coating's anticorrosion properties (Kalendova, 2003). Zinc powder is among those significant non-toxic metal pigments (Barranco *et al.*, 2004), which has barrier and electrochemical mechanism protection (Prokes and Kalendova, 2007). Zinc-rich coatings and modified zinc coatings have been demonstrated as an effective coating more than other coating types (Evans and Mayne, 1944), (Feliu *et al.*, 1989), (Feliu *et al.*, 1989), (Morcillo *et al.*, 1990), (Pereira *et al.*, 1990), (Arman *et al.*, 1992), (Fragata *et al.*, 1993), (Real *et al.*, 1993), (Abreu *et al.*, 1996), (Abreu *et al.*, 1999), (Feliu *et al.*, 2001) and (Vilche *et al.*, 2002). Their successness are measured based on their particular power to give cathodic protection which is sacrificial action of the zinc (Weldon and Carl, 1997) and to act as a resistant barrier where the protecting film was sealed by zinc white corrosion products (Parashar *et al.*, 2001). The nature of this barier has been subject to the researchers over many years in the field of protective organic coatings. The early assumption was that the organic coating acts as a barrier to water and oxygen from the surrounding (Thomas, 1991). However, throughout the research that had been done over the last half century have proved that their resistance to the flow of ionic current is the limiting factor in the protective mechanisms of barrier coatings (Dickie and Smith, 1980).

2.4.1 Zinc Corrosion Products

The reaction of zinc metal with oxygen, water and carbon dioxide present in the air produced the corrosion products like zinc oxide, zinc hydroxide and zinc carbonate. Exposed zinc metal combines with oxygen to form a very thin layer of zinc oxide. The formation of zinc hydroxide is from the reaction of zinc metal with water. The final corrosion product is zinc carbonate resulting from reaction of zinc hydroxide with carbon dioxide in the air. These products are very meaningful since it's able to excellently seal all pores in the coating material (Kalendova *et al.*, 2015).

Figure 2.5.1-1 shows a very compact and perfectly adhering barrier layer that is highly resistant to normal atmosphere effects emerges. This even represents active protection because of the renewal of the function of electrochemical cathodic protection after each instance of mechanical damage to the film (Kalendova, 2003) and (Schaefer and Miszczyk, 2013). Zinc oxide and zinc hydroxide also show some anticorrosion properties (Arman *et al.*, 2013). While zinc carbonate is a thin and stable (insoluble in water) layer that provides protection to the underlying zinc. This is the primarily reason for its low in corrosion rate in most environment (ASTM, 2006).



a) Magnification 8000×

b) Magnification 4000×

Figure 2.4-1: Corrosion changes on the surface of the coating material pigmented with zinc (spherical particles)

Source: (Kalendova et al., 2015)

Figure 2.5.1-2 shows the first phase of protection is electrochemical reaction alone. After some time, a layer of oxide which is zinc oxide will coating zinc particles in the coating materials, cause the conductivity of the zinc reduced. The corrosion product prevents zinc to corrode and hinders the electrochemical role of zinc. The content of zinc oxide in the film can be up to 20% without decreasing its efficiency of protection, because of a certain conductivity of the zinc oxide (Kalendova, 2003) and (Schaefer and Miszczyk, 2013). The efficient cathodic protection at the first stage was changed to the protection that is secured by a mere barrier effect. The zinc oxidation products sealed the pores between zinc particles until reaching the system becomes nonconductor (Kalendova, 2003). The paint coating then consists of zinc particles, a very small amount of binders and zinc oxide that seals the pores.



Figure 2.4-2: Electrochemical phase of zinc action in a coating

Source: (Kalendova et al., 2015)

2.5 PIGMENT VOLUME CONCENTRATION (PVC)

Concentration of zinc powder in coating materials just near CPVC (critical pigment volume concentration) provide substrate protection through electrochemical reaction in the region of cathodic (Kalendova *et al.*, 2015). PVC (pigment volume content) is called CPVC when the pigment and binder blend begin to create voids that increase porosity. In other words, CPVC is PVC at low value. PVC was formulated as below:

$$PVC = \frac{V_b + V_p + V_f}{V_p + V_f}$$

(Equation 1)

In order to provide electric conductivity between adjacent particles as well as between the pigment particles and the substrate, a high pigment concentration is necessarily needed, so that it will packed closely enough in the dry film. This allows the zinc-steel galvanic couple to generate the conduction of electric current during electrochemical reaction (Lindquist *et al.*, 1985) and (Romagnoli and Vetere, 1992). As a result, a very porous film will be obtained. Therefore, it will be able to absorp the penetrating solution (Shreepathi *et al.*, 2010). The paint is considered high PVC paint when the value of PVC is 50 or higher. This means that the coating content is more pigment and less binder, thus the film becomes less adhesive and more porous.

In organic coatings, a crosslinking (curing) reactions forming a highly crosslinked polymeric film, and a binder also presents to coat the zinc particles. The resistivity of the coatings is increased to the point where its electrical conductivity decreased below the critical level even until the coating material does not provide electrochemical protection anymore (Buxbaum, 1998). Therefore, the electric conductivity of pigmented film is related to the PVC of the zinc in the coating material binder. Zinc particle is efficient at concentration of 94-96% (w/w) in paints (Leclerq, 1991). Another researcher claims that this pigment achieved the highest electric conductivity at concentration ranging from 94% to 96% with binder content at 5-8% in paints (Arianpouya *et al.*, 2013). However, this requirement comes with several problems. Such low binder content is insufficient to attain the required physiomechanical properties like adhesion, impact resistance and cupping resistance (Arianpouya *et al.*, 2013). Physico-chemical properties and corrosion resistance of zincrich coating are depend on the PVC, shape and size of zinc dust (Vilche *et al.*, 2002) and (Abreu *et al.*, 1997).

It is well known that the ratio of PVC to CPVC should be less than 1. Higher value of this ratio will influence the mechanical and permeability characteristics of the coating (Ahadi and Attar, 2007). However, formulator keeps the ratio more than 1 because the sacrificial action of zinc occurs only when there is continuous contact between metal particles (percolation path) (Nanna and Bierwagen, 2004).

A zinc content higher than 60% by weight is recommended to give a good protection (Fragata *et al.*, 1987), (Feliu *et al.*, 1989), (Romagnoli and Vetere, 1992), (Abreu *et al.*, 1997) and (Morcillo, 1999). Under immersion conditions, the time of cathodic protection depends on the zinc content in the coating film, and they verified coatings with 60 volume percent of zinc powder showed good corrosion resistance mainly due to the cathodic protection. Later on, some researchers stated that the zinc volume of 65% and above (more than or equal to 90% by weight on dry film) will build a reliable percolation (Marchebois *et al.*, 2002), (Nanna and Bierwagen, 2004) and (Bierwagen *et al.*, 2007). (Shreepathi *et al.*, 2010) clearly stated based on EIS studies that percolation limit for providing sufficient galvanic protection was attained at 70% zinc on dry film. When the zinc content in the coatings excess 80%, superior galvanic protection is achieved. However, coating containing 40% of zinc content also shows very good protection mechanism mainly from epoxy resin as a binder. Actually, the efficiency of the coating is not about how much the content of the zinc dust used in the formulation, but how many percent the purity of the zinc itself.

2.6 FLY ASH AS AN EXTENDER PIGMENTS

There were some studies to substitute zinc with other pigments in coating materials, mainly for financial and environment reasons (Guidice *et al.*, 2004) and (Armelin *et al.*, 2010). Extender pigments are included in the coatings as spacers to lower the galvanic action (zinc consumption) and the cost consumed. The presense of these pigments in the coatings did not affect the anticorrosive performance. The low content of zinc in the coating had been improved coatings behaviour by the addition of extender pigments (Fragata *et al.*, 1993). The existence of extender pigments in the coating film actually does influenced the behaviour of the coatings with respect to the corrosion potential variations. Conductive pigment that added as the extender pigment will improve the percolation (Marchebois *et al.*, 2002).

Table 2.7-1 below shows a normal range of chemical composition for fly ash produced from different coal types, expressed as percent by weight. Silica and alumina both have highest percentage which gives a good abrasion resistance, electrical insulation and high thermal stability. While alumina has a better wear resistance.

Component	Bituminous		Subbitumin		Lignite
				ous	
SiO ₂	1	20-60		40-60	15-45
Al ₂ O ₃		5-35	-	20-30	10-25
Fe ₂ O ₃		10-40	-	4-10	4-15
CaO		1-12		5-30	15-40
MgO		0-5		1-6	3-10
SO ₃		0-4		0-2	0-10
Na ₂ O ₃		0-4		0-2	0-6
K ₂ O		0-3		0-4	0-4
LOI		0-15		0-3	0-5

 Table 2.6-1: Normal range of chemical composition for fly ash produced from different coal types

Source: (User guidelines for waste and byproduct materials in pavement construction, 2016)

(Kotnarowska, 1997) revealed that 10 wt % glass microspheres produced from fly ash with epoxide coating has the highest resistance to erosive wear because of dissipation energy released during collasion by the composite. The differentiated diameters and shapes of filler also gave effective filling of internal voids in the structure of the cotings, thus lowering the porosity of the coating. Therefore, the mechanical properties and thermal resistance improved, while the ability of the coating to absorb water and aggressive agents reduced. Figure 2.7-1 shows a morphology of glass microspheres with magnification of 1000 times.



Figure 2.6-1: Morphology of glass microspheres (magnification 1000 times)

Fly ash from coal consist of microscopic flakes and hollow spheres of mullite $(3Al_2O_32SiO_2)$ which have excellent corrosion resistance, high thermal stability and low thermal conductivity (Morquecho *et al.*, 2012). These properties proved that fly ash is a promising material as a coating. Fly ash also can reduced the density of coating, with the cenospheres in the fly ash that provides added buoyancy, better insulation properties, reduced shrinkage and warp age value (Wandell, 1996).

2.7 ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

EIS is widely used to evaluate the efficiency of organic coatings and the mechanism of corrosion resistance (Kalendova *et al.*, 2006). In Bode modulus diagram of EIS, a high performance barrier coating gives a straight curve with unit negative slope (pure capacitive action). Modulus of impedance digresses from its straight line path, when solutions penetrate through the coating followed by corrosion initiation. Much literature suggests that when the resistance of the coating (low frequency impedance) is $< 10^7 \Omega$ cm² then such coatings are not protective (Leidheiser, 1979), (Leidheiser, 1991) and (Gray and Appleman, 2003). Such judgment of EIS data can mislead a paint formulator who does not have good knowledge in electrochemistry. An appropriate example in this case is a ZRP (>90% zinc on dry coating) having superior

corrosion resistance properties exhibits low frequency. The influence of the zinc content on the paint behavior has been studied, but little attention has been paid to steel/paint interfacial contamination, which simulates practical application conditions. This work will evaluate the corrosion behaviors/performances of zinc rich paint (ZRP) applied on steel substrates under NaCl solution as artificial seashore environment by using Open Circuit Potential (OCP) and Electrochemical Impedance Spectroscopy (EIS).



CHAPTER 3

METHODOLOGY

3.1 INTRODUCTION

This study will be divided into 3 phases. The first phase is formulation of coating based on various pigment volume concentration. Following with thickness inspection and evaluation of mechanical and electrochemical properties for phase 2. Lastly for phase 3, the coating performance will be measured.





Figure 3.1-1: Process flow diagram for organic zinc coating

3.2 PRETREATMENT OF METAL SUBSTRATE

In this study, the substrates used for all coating substrates are a pure iron sheets (Fe 99.5%). The iron sheet is cut into (10mm X 20mm X 0.5mm) in dimension. The metallic substrates were first serially polished with sand papers #180, #220, #280, #600, #800, #1000 and #1500 to produce mirror like surface like in Figure 3.3-1. Figure 3.3-2 shows the metal substrates were then introduced into ethanol and rinsed using an ultrasonic bath. Ethanol is employed to degrease the surface of the metal substrates. The clean substrates then, dried in the oven at 60°C as shown in the Figure 3.3-3 before proceed to the next stages.



Figure 3.2-1: Metallic substrates after polished with sand papers



Figure 3.2-2: The metallic substrates were ultra-sonicated with ethanol to degrease the surface of the metal



Figure 3.2-3: Drying of the metallic substrates in the oven

Copper wire was cut 10 cm long and then soldered on the substrate plate. Copper wire is being used because it can conduct electricity during a corrosion test. After that, epoxy resin was mounted on the soldered part to strengthen the adhesion of copper wire on the substrate plate. Figure 3.3-4 and Figure 3.3-5 show the soldered metal with copper wire and mounted metal with epoxy resin respectively. The substrates with mounted epoxy resin were dried at room temperature for 6 to 7 hours. The dried samples were stored in the oven at 60 \degree to avoid corrosion on the uncoated plates.



Figure 3.2-4: The metallic substrates after soldered with copper wire



Figure 3.2-5: The metallic substrate mounted with epoxy resin

3.3 PRETREATMENT OF FLY ASH

Fly ash was used as an extender pigment or filler in this study. Fly ash that comes from industry was a bit wet. Therefore, drying process was required. Fly ash was dried in the oven at $60 \,^\circ$ C for 20 minutes. After that, the dried fly ash was undergoing grinding process to reduce the size of the fly ash. Figure 3.4-1 and Figure 3.4-2 show the fly ash before grinding process and after grinding process respectively. Sieve shaker was employed to filter the bigger size of fly ash. Mastersizer was being used to indicate the size distribution of fly ash. A very fine fly ash was used to identify the chemical component content by using Fourier Transform Infrared Spectroscopy (FTIR).



Figure 3.3-1: Fly ash before grinding



Figure 3.3-2: Fly ash after grinding

3.4 FORMULATION OF PAINT

A lot of researchers claimed that paint with 60% PVC give great protection towards corrosion. Therefore, the formulation of paint was started at 60% PVC. Since the adhesion of this formulated paint was so bad at 60% PVC, the new formulation with variation of PVC values were implemented.

For preliminary data, kaolin was used as an extender pigment instead of fly ash and the composition of kaolin was fixed at 5% from PVC value. Table 3.5-1 shows a formulation of paint with kaolin as a preliminary observation.

Pigment	Epoxy	Zinc	Kaolin	Ethanol	Zinc	Kaolin
Volume	Resin (g)	Oxide	(g)	(mL)	Content	Content
Concentration,		(g)			(w/w %)	(w/w %)
PVC (%)						
60	5.5	40.81	2.11	25	84	4.36
50	1	4.97	0.27	6	78	4.33
40	1.8	5.9	0.31	4.5	74	3.87
30	2	4.2	0.22	2.8	65	3.43
20	1.54	1.91	0.1	1.6	54	2.82
10	3	1.59	0.09	1	34	1.92
			VIE	-		

Table 3.4-1: Ingredients in the formulated paint with 5% kaolin

3.5 PAINTING TECHNIQUES

After the substrate was properly cleaned and dried, it is then ready for the painting process. We employed 'dry-on-dry' technique, in order to have a smooth coating surface on the metallic plates. In this technique, one coat is painted and the next coat will apply after the previous coat dry completely. The thickness of coating on the substrates was varied based on the layer of coating that being applied (1, 3 and 5 layers). Painting process is conducted in the temperature ranges between 20-25°C to achieve optimum and similar coating. While painting, the amount of paint that being used for coating. After that, the samples will be dried at ambient temperature for 1-2 hours.

3.6 SURFACE MORPHOLOGY AND COMPOSITION BY SCANNING ELECTRON MICROSCOPE (SEM)

Morphology of the coated substrate is studied using Field Emission Scanning Electron Microscope (FE-SEM) fitted with Energy Dispersive Analysis X-ray (EDAX) for chemical composition analysis of the coating.

3.7 ELECTROCHEMICAL POLARIZATION CURVE MEASUREMENTS

Corrosion behaviour of coated substrate at various coating thickness will be studied using electrochemical polarization curve measurements. In order to investigate the electrochemical behaviour of the coated substrate polarization measurement will be performed using electrochemical measurement system. The coated substrate sample is used as the working electrode. Platinum electrode is employed as a counter electrode, and Ag/AgCl/KCl (saturated) is used as a reference electrode. Then, all the three electrodes were connected to the test solution or electrolyte (NaCl solution). Polarization curve measurements of a sample are obtained in 3 wt./wt. % NaCl solution from -1.0V to 1.0V.



CHAPTER 4

RESULTS AND DISCUSSION

4.1 INTRODUCTION

This chapter presents a comprehensive study to evaluate the efficiency organic coating on coated carbon steel and the effect of using epoxy, zinc oxide and zinc rich spray paint. The expected result discussed was about the physical test include adhesion test, immersion test, thickness and internal behaviour using SEM analysis for morphology observation.

4.2 ADHESION OF COATING ON THE METALLIC SUBSTRATE

Figure 1 shows the visual performances for surface of metallic substrate after being coated. The glossy look on the surface of coatings increase as the pigment volume concentration (PVC) increase. 10% PVC with 5 layers of coating, shows the glossiest among others. These glossies came from the properties of epoxy resin. Since the 10% PVC has the most binder content, therefore it came as the glossiest coating. As the glossiness reduced, the cracking of paint slowly appeared on the surface of coatings.

Starting from 40% PVC until 60% PVC, the coatings obviously loss its adhesion on the substrate. The crack on the coatings appeared because of the high content of the pigments. The size of the crack increased as the layer of coating increased. 60% PVC shows the worst of adhesion with the 5 layers of coating does not adhered at all.



Figure 4.2-1: The coatings with 10% vol/vol (kaolin/pigments). The layer of coating from left to right is 1, 3 and 5. (A is the coating with 10% PVC, B is the coating with 20% PVC, C is the coating with 30% PVC, D is the coating with 40% PVC, E is the coating with 50% PVC and F is the coating with 60% PVC).

The percentage of pigments content in formulated paints are displayed in Table 4.2-1. Too much pigments content in the paints lead it to the cracking surface thus make it loss in adhesion. This formulated paint can only bear up to the 68.85% of pigments content by weight. Approximately 70% pigments content and above by weight obviously shows that this paint lack of binder to hold the paint on the metallic surface of substrate.

Because of the loss of adhesion on the coatings with 40% PVC to 60% PVC, therefore these coatings will not undergo the corrosion test.

Pigment		Zinc	Kaolin	Total	
Volume		Content	Content	Pigments	
Concentration	n,	(w/w %)	(w/w %)	Content	
PVC (%)				(w/w%)	
60		84	4.36	88.64	
50		78	4.33	83.97	
40		74	3.87	77.53	
30		65	3.43	68.85	
20		54	2.82	56.52	
10		34	1.92	35.90	

Table 4.2-1: Percentage of zinc and kaolin content in the formulated paint

4.3 IMMERSION TEST IN SODIUM CHLORIDE SOLUTION

After 30 days of immersion in NaCl solution, coatings with commercial spray showed an obvious different patterns of corrosion on coated surface. T1-layer of coating had white corrosion product and some brown rust on the surface of the coating. The white corrosion product was all over the surface of coating and sealed the cut which located on the center of the coating. Basically, the white corrosion product was from commercialized spray, while the brown rust was from production of corrosion from the steel. Commercialized spray had an active corrosion pigment and cathodic protection behavior to block or seal the steel from corroded by using its corrosion (Zn(OH)₂ or ZnO) will grow as a result of the oxidation of zinc particles. However, the existence of brown rust on the surface of coating proved that1-layer coating was too thin and insufficient to protect the steel from corroded (Figure 1 (a)). It showed that the strong diffusion of iron corrosion products from the steel to the top of coating had occurred (Shi *et al.*, 2011).

The white color of corrosion product appeared on the surface of 3-layers of coating. The white color of corrosion product seems perfectly sealed on the cut part. A

very little of brown rust on the upper side of coating comes from the back side of the steel because it is not covered by the spray (Figure 1 (b)). It showed that commercialized spray protects the steel from corrosion by its two different mechanisms. The first one is by sacrificial cathodic protection. The active pigment inside the spray sacrificed itself to corrode. Secondly, after the corrosion of active pigment from the spray, its white corrosion product which is the oxide layer will seal the pores on the surface of coating. This is called as barrier protection. The nature of this barier has been subject to the researchers over many years in the field of protective organic coatings.

The 5-layers of coating showed the worst. There were white and brown corrosion product from the spray and steel respectively (Figure 1 (c)). The brown rust covered the cut part. It showed that there was not enough barrier protection from the white corrosion product. As shown in Figure 1 (d), the coating was swollen and the surface of coating was broken. This proves that too much coated will make the coating available to absorb the water from the solution, thus make it penetrate through the surface of the steel and corroding the steel. The absorption of penetrating solution occurred on the porous film (Shreepathi *et al.*, 2010).



Figure 4.3-1: The commercial spray after 30 days immersed in NaCl solution. ((A) 1 layer (S1), (B) 3 layers (S2), (C) 5 layers (infront view) (S3) and (D) 5 layers (side view) (S3)).

Figure 4.3-1 showed the brown color of steel corrosion product appeared only on the sides of the steels. This is from the corroded steel at the back of the substrate. On the surface of the coating with 30 % PVC (Figure 4.3-1 (A)), there were some changes in color of coating. While for 20 % and 10 % PVC (Figure 2 (B) and (C)), the color of the coating still remains the same. There was no swollen coating as commercialized

spray. The existence of more pigments than epoxy resin in the paint gave a porous surface to the coating of 30% PVC. Since the total pigments percentage not exceed 70% by weight, therefore the porosity on the surface of the coating was not severe. The epoxy resin still capable to cover up the pores. While for 20% and 30% PVC, obviously the epoxy resin was being a protector than the pigments itself. These formulation does not need cathodic protection from the zinc because epoxy resin used its barrier protection to protect the steel from being corrode. Previous study (Shreepathi., 2010) proved that formulation with low zinc content provided good barrier protection which came from epoxy resin.



Figure 4.3-2: The formulated paint after 30 days immersed in NaCl solution. (a: 30% PVC, b: 20% PVC and c: 10% PVC). (From left to right: 1, 3 and 5 layers of coating).

4.4 MORPHOLOGICAL STUDIES

The SEM micrographs of less corroded sample before and after immersed in NaCl solution for commercialized spray and formulated paint are shown in Figure 3.

The results show that the particles of an active pigment in commercialized spray (S2) are appropriately in contact with each other. The size of particles is varying, showing that there is an extender pigments in the spray. The presence of multiple

particles size thus reducing the voids space. Figure 4.4-1 (B) showed that the corrosion products had covered and sealed the voids. It is expected that the size differences of particles in commercialized spray lead to a better packing, causing enhancement of barrier properties of the commercialized spray. While for sample P9, the particles cannot be observed clearly because of the layer of epoxy resin. The particles were covered and hold by epoxy resin. Figure 4.4-1 (D) showed that there are no corrosion products to cover the particles. Based on Figure 4.4-1, it can be seen clearly that sample S2 protects the steel with its cathodic protection and then barrier protection. Sample P9 showed that it had a barrier protection came from epoxy resin which enclosed the surface of the substrate. In this case, the zinc particles inside this formulated paint does not functioning it cathodic properties unless the NaCl solution is being absorb in the coating towards the metallic substrate, because the epoxy resin had over taken the protection by its barrier protection.

From Figure 4.4-2, the cross sectional for sample P9 showed the coating consist of microscopic flakes and hollow spheres of mullite (3Al₂O₃2SiO₂) which from kaolin. It has excellent corrosion resistance, high thermal stability and low thermal conductivity (Morquecho *et al.*, 2012). These properties proved that kaolin is a promising material as a coating. Based on Figure 4.4-2 (B), there is no corrosion product appeared in the coating. This strengthen the claim that epoxy resin provided good adhesion and corrosion resistance (Ashraf *et al.*, 2015).



Figure 4.4-1: SEM micrographs before and after 30 days of immersion in NaCl solution. ((A) commercialized spray (S2) before immersion test; (B) commercialized spray (S2) after immersion test; (C) formulated paint (P9) before immersion test; and

(D) formulated paint (P18) after immersion test.)

ИP



Figure 4.4-2: SEM micrographs of sample P9 (cross sectional) before and after 30 days immersion in NaCl solution. ((A) before immersion; and (B) after immersion.)

4.5 POLARIZATION TEST IN NACL SOLUTION

Corrosion potential were recorded as a function of current density to evaluate the ability of cathodic protection of the coatings. The protection of steel from zinc rich paint was experimentally standardize the corrosion potential more negative than -0.78V (Shi *et al.*, 2011). Above this potential, the coatings simply act as a barrier layer. Figure 4.5-1 to Figure 4.5-4 show the evaluation of the corrosion potentials of commercialized spray, formulated paint of 10%, 20% and 30% PVC at different layers of coating with current density.

According to Figure 4.5-1, commercialized spray showed that it had cathodic protection from the active pigments. The highest E_{corr} (more negative) was -0.975V from 5 layers of coating, thus making it less noble. The active pigments in the commercialized spray actively corrode to form white corrosion products.

While for all formulated paints (Figure 4.5-2 to Figure 4.5-4), the corrosion potential was in between -0.4 to -0.5V making it less sacrificial than commercialized spray. However, the formulated paint of 10% PVC (Figure 4.5-2) the 5 layers of coating had the lowest current density approximately 1.5×10^{-8} A/cm² which lower than commercialized spray. The low value of current density basically showing that coating also can behave as a good protection from steel corrosion. This low value of current

density mainly come from barrier protection of epoxy resin (Shreepathi *et al.*, 2010). The lower zinc content in the formulated paints make it the lower galvanic action (Fragata *et al.*,1993). Therefore, these formulated paints behave as a barrier protection. The shape of the experimental curve for 10% PVC with 5 layers of coating indicates that the working electrode passive spontaneously when immersed in the corrodent at E_{corr} -0.5V. The current increased sharply indicates that induced anodic polarization to 1.0 V (potential) was insufficient to result in pitting.

PVC of 30% (Figure 4.5-4) showed that the trend of polarization curve obviously differs from others. In this case, the E_{corr} was in between of -0.4 to -0.5V. The subsequent polarization curve in the more positive direction from E_{corr} in between 0 to -0.2V was from localised corrosion (Flitt and Schweinsberg, 2005). This means that the substrate undergoes spontaneous passivation in the corrodent and followed by induced pitting.



Figure 4.5-1: Polarization measurement of commercialized spray



Figure 4.5-2: Polarization measurement of formulated paint (10% PVC)



Figure 4.5-3: Polarization measurement of formulated paint (20% PVC)



Figure 4.5-4: Polarization measurement of formulated paint (30% PVC)

Table 4.5-1 showed the electrochemical properties and corrosion rates of the sample. A system's polarization resitance, R_p , was calculated by using the Stern-Geary equation (Equation 2). While Equation 3 was used to calculate corrosion rate in terms of penetration rate, \bar{v}_p .

$$R_{p} = \frac{B}{i_{corr}}$$
(Equation 2)
$$\tilde{v}_{p} = \mu_{eq} K_{p} \frac{i_{corr}}{\rho}$$
(Equation 3)

According to Table 4.5-1, P18 had the lowest current density with the lowest corrosion rate. Its corrosion rate was lower than commercialized spray even though it had less negative E_{corr} value. This show that barrier protection from the epoxy resin much better than cathodic protection from an active pigment in commercialized spray. Table 3 clearly showed that as the amount of epoxy resin increased, the corrosion rate also increased.

Sample	Anodic	Cathodic	Proportionality	Current	Linear	Corrosion
	Slope, Ba	Slope, Bc	Constant, B	Density,	Polarization	Rate
				Icorr	Resistance,Rp	(mm/yr)
				(A/cm^2)		
S1	2962.96	1666.67	463.77	5.40 X 10 ⁻⁶	8.59 X 10 ³	0.063
S2	2003.82	1521.74	376.05	5.00 X 10 ⁻⁶	7.52×10^3	0.058
S3	2403.85	1875.00	457.99	5.30X 10 ⁻⁷	8.64 X 10 ⁴	0.0062
P10	284.20	1200.00	99.90	3.80X 10 ⁻⁶	2.63 X 10 ³	0.044
P11	482.85	275.86	76.33	3.25X 10 ⁻⁶	2.35×10^3	0.038
P12	793.65	307.69	96.40	3.20X 10 ⁻⁶	3.01 X 10 ³	0.037
P13	300.17	483.33	80.51	4.50X 10 ⁻⁶	1.79 X 10 ³	0.052
P14	314.25	261.90	62.11	3.20X 10 ⁻⁶	1.94×10^3	0.037
P15	84.32	888.89	33.48	5.50X 10 ⁻⁶	6.09×10^3	0.064
P16	557.77	628.14	128.45	2.70X 10 ⁻⁶	4.76×10^3	0.031
P17	327.46	1025.64	107.92	2.00X 10 ⁻⁶	5.40×10^3	0.023
P18	173913.00	606750.10	58769.30	1.50X 10 ⁻⁸	3.92 X 10 ⁸	0.00018

UMP

 Table 4.5-1: Electrochemical parameters and corrosion rates

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

The corrosion behavior of the formulated paint and commercialized spray on the metallic substrate has been studied. The 30 days immersion test in NaCl solution show that the formulated paints protect the steel by barrier protection while commercialized spray by cathodic protection and followed by barrier protection. The white corrosion product grew on the surface of the commercialized spray to seal the pores on the coating surface. Polarization measurement indicate that the corrosion potential of formulated paints less negative than commercialized paint and prove that commercialized spray less noble than formulated paints. This work suggests that the best layers of coating or thickness, should be 5-layers to avoid insufficient protection and penetration of water from the solution.

5.2 **RECOMMENDATION FOR FUTURE WORKS**

The application work is limited by using small sample plate only for laboratory research without dealing with real parts of pipeline in the plant. For more advanced, recommend using a large plate or large pipe instead small plate immersed in the sea about 2 months and see the effect of corrosion.

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